

Simultaneous Enhancement of Toughness and Strength of Stretched *i*PP Film via Tiny Amount of β -Nucleating Agent under “Shear-free” Melt-extrusion

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Electronic Supplementary Information

Abstract Herein, isotactic polypropylene films with small β -nucleating agent content were fabricated via a melt-extrusion-stretched technology with intended “shear-free” in barrel and die. Compared with neat films, the tensile strength, elongation at break and strain energy density at break of *i*PP film with 0.05 wt% β -nucleating agent are significantly improved by 13.8%, 39.6% and 90.6%, respectively, indicating the simultaneously enhanced toughness and strength. Additionally, the β -crystal content gradually increases with increasing β -NA content, while the relative total daughter content of α - and β -crystal exhibits opposite tendency. Moreover, nucleation and crystal growth induced by various β -NA contents are different. This work proves an efficient strategy to enhance mechanical properties of isotactic polypropylene film via controlling elongation flow and addition of appropriate β -NA content.

Keywords Melt-extrusion; Isotactic polypropylene; β -Nucleating agent; Crystallization; Mechanical properties

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INTRODUCTION

Commercial isotactic polypropylene (*i*PP) with at least four basic crystalline modifications, *i.e.*, monoclinic α -crystal, trigonal β -crystal, orthorhombic γ -crystal and smectic mesophase,^[1,2] is a classic thermoplastic with tremendous industrial application value due to its excellent comprehensive properties. Among the above crystalline phases, β -crystal shows the excellent toughness and ductility, and thus attracts the most academic interest and industrial applications. Nevertheless, its formation needs certain conditions, including abrupt temperature gradient,^[3] elongation or shearing deformation^[4–6] and β -nucleating agent (β -NA).^[7] Among the above approaches, the introduction of β -NA is regarded as the most efficient and reachable strategy.

During practical polymer processing, there exists elongation/shear flow fields, which profoundly affects orientation, nucleation and consequent crystallization of polymer.^[8,9]

However, unlike “weak” shear flow field, elongation is much more effective in promoting the formation of oriented structures and thus enhancing tensile strength.^[10] Naturally, the combination of β -crystal generated via β -NA and orientation crystallization induced by stretching is supposed to be capable of simultaneously reinforcing and toughening *i*PP parts. In fact, due to complicated flow field in practical extrusion process, it is not easy to be realized.^[11] During practical extrusion process, there is a complicated and inevitable stretching flow field, including shearing in extrusion barrel or die and stretching after leaving the die exit. However, the influence of stretching in extrusion barrel or die on orientation crystallization is not clear. Herein, to tremendously reduce flow field in barrel and die, the speed of screw rotation was slowed down to 0.6 r/min, which is different from that in literature.^[11,12] Therefore, stretching after leaving the die exit can be considered as principal factor manipulating orientation crystallization in samples.

The major aim of this study is to investigate the evolution of crystallization behavior and mechanical properties upon various β -NA contents and strong elongation flow field. Furthermore, the relationship between crystallization structure

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and tensile properties is established. Noting that β -crystal content gradually increases with the augment of β -NA content even though the elongation flow field is relatively strong. Interestingly, the tensile properties of *i*PP film containing 0.05 wt% β -NA is higher than those of other films, indicating the simultaneously enhanced toughness and tensile strength.

EXPERIMENTAL

Materials

Commercial *i*PP (T30S) used in this work was purchased from Lanzhou Petroleum Chemical Co., China. Its $\overline{M}_w$ and melt flow index are 1.1×10^5 g/mol and *ca.* 2.6 g/10min (190 °C, 21.6 N), respectively. The β -NA (trade-marked as WBG-II), was purchased from Guangdong Winner Functional Materials Co., Ltd. WBG-II is a heteronuclear dimetal complex of lanthanum and calcium with some specific ligands. Its general formula is $\text{Ca}_x\text{La}_{1-x}(\text{LIG1})_m(\text{LIG2})_n$, where *x* and 1−*x* are the proportion of Ca^{2+} and La^{3+} ion in the complex, respectively, while LIG1 and LIG2 are, respectively, a dicarboxylic acid and amide-type ligand with coordination number of *m* and *n*. As shown in our previous work,^[13] the length and diameter of a single raw β -NA are *ca.* 1 μm and tens of nanometers, respectively.

Sample Preparation

The *i*PP pellets and various β -NA contents were blended in a twin screw extruder (SHJ-20B). During blending process, the temperatures were 150, 160, 170, 185, 195 and 190 °C from hopper to die. Subsequently, the pelletized and dried droplets were extruded *via* a single screw extruder (*i.e.*, Haake PolyLab System-Rheomex 252p series) through a slit die (1×50 mm). Moreover, temperature profiles were 165, 180, 195 and 185 °C from hopper to die, respectively. For the sake of minimizing shear stress in die, screw speed of extruder was controlled at 0.6 r/min. Therefore, melt flow rate in die was exceedingly small (*ca.* 0.9 cm/min) and thus the influence of shear stress can be ignored. During the extrusion process, *i*PP or β -nucleated *i*PP melt was stretched under a constant stretching rate of 90 cm/min once it left die exit of extruder. Schematic of films process and a typical photo of them are presented in Figs. S1(a) and S1(b) (in the electronic supplementary information, ESI). All take-up rollers were kept at *ca.* 25 °C (*i.e.*, room temperature). For simplicity, the obtained films were named as *i*PP90-*y*, where *y* refers to β -NA content. The thickness of melt-stretched films is about 28–30 μm .

Characterizations

Mechanical properties

Mechanical performances of specimens were assessed *via* a SUNS Universal tensile testing machine. According to ASTM D638-03, the crosshead speed was set at 30 mm/min. During the testing process, the gauge length of samples was 16 mm. All dumbbell-shaped specimens (see Fig. S1c in ESI) were cut in the center of above films using a cutting knife along stretching direction. For every composition, at least five specimens were tested and the experimental results of tensile parameters were evaluated as average of them.

X-ray measurements

Two-dimensional small-angle X-ray scattering (2D-SAXS) and two-dimensional wide-angle X-ray diffraction (2D-WAXD) experi-

ments were conducted in Shanghai Synchrotron Radiation Facility (SSRF). A MAR 165 CCD X-ray detector was used for collection of 2D-SAXS and 2D-WAXD images. The chosen X-ray wavelength and X-ray resolution of this detector were 0.124 nm and 2048 pixel × 2048 pixel, respectively. The distance between this detector and sample for X-ray measurements was 5200 mm and 178 mm for 2D-SAXS and 2D-WAXD, respectively. Moreover, several pieces of *i*PP or β -nucleated *i*PP films were accumulated orderly with final thickness of *ca.* 1 mm so as to get maximum diffraction intensity. All the data were treated with FIT2D software.

Differential scanning calorimeter (DSC)

A DSC (TA-2920) instrument was employed to study the melting and crystallization behaviors of films. The DSC measurements were carried out in nitrogen atmosphere. As illustrated in Fig. S1(b) (in ESI), specimens (*ca.* 6 mg) were heated at a heating rate of 10 °C/min from 25 °C (*i.e.*, room temperature) to 200 °C. To eliminate the heat history, specimens were kept for 5 min at 200 °C and then cooled at the same cooling rate of 10 °C/min.

Atomic force microscopy (AFM)

An AFM (Bruker, Multimode 8) was employed to observe the topography of films in tapping mode. All experiments were performed in air at about 25 °C (*i.e.*, room temperature). All the data were treated with NanoScope Analysis1.5 software. The crystalline morphologies distinguished from height and amplitude images were collected.

Polarized optical microscopy (POM)

The morphology development of films during non-isothermal crystallization was investigated *via* a POM (Olympus BX-51). Specimens for POM observation were cut from the center of films. These specimens were placed in the hot stage, and each was heated to certain melting temperature and kept for 5 min at this temperature. Then, the specimens were cooled to 40 °C at a cooling rate of 10 °C/min, and thus during non-isothermal crystallization process, the crystallization morphology was recorded *via* POM. For comparison, the crystallization morphology development at the same conditions of *i*PP film prepared at relatively lower stretching rate was observed, and the results are shown in Fig. S6 (in ESI).

RESULTS AND DISCUSSION

Mechanical Properties of Films

Fig. 1 shows the typical stress-strain curves and quantitative estimated mechanical properties (strain energy density at break, W_b ; tensile strength, σ ; elongation at break, ϵ) of films. As well known, σ of *i*PP is about 35 MPa.^[12,14,15] Herein, σ for all films is higher than 50 MPa. In addition, compared with *i*PP90-0, both ϵ and W_b of β -nucleated films are improved significantly. Unexpectedly, σ , ϵ and W_b of *i*PP90-0.05 are 68.5 MPa, 1064% and 524.1 MJ/m³, respectively, which are the maxima. Nevertheless, σ of *i*PP90-0.2 is higher than that of *i*PP90-0.1. Since tensile properties of samples are mainly influenced by their microstructure, in the following scenario, systematic characterizations will be conducted to investigate thoroughly the correlation between tensile properties and microstructure.

Crystalline Structure

Fig. 2 shows the 3D-WAXD, 3D-SAXS images and their

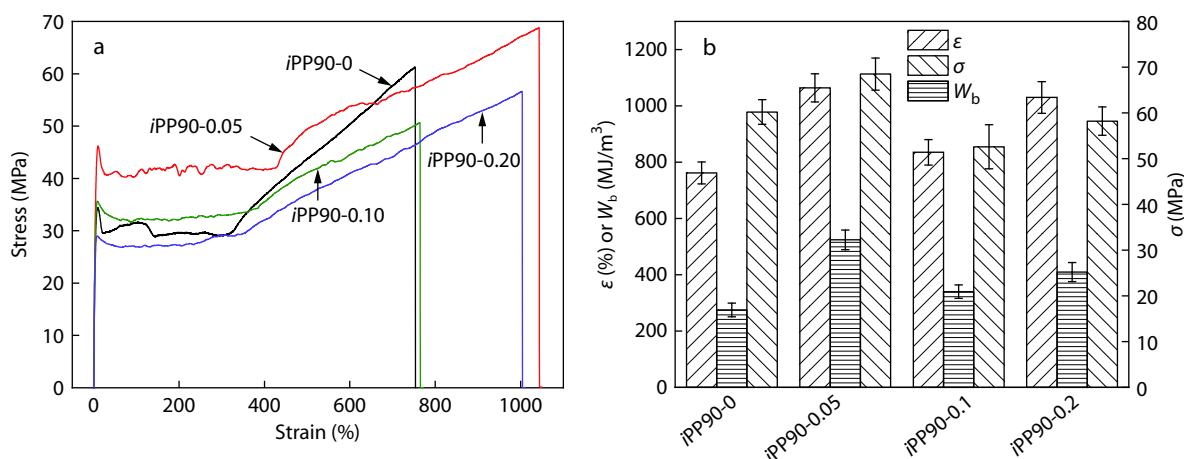


Fig. 1 (a) The typical stress-strain curves and (b) tensile properties for films.

corresponding curves of films. As can be seen, evident arc-like diffractions of lattice plane (Fig. 2a) and an intensive two-spot pattern in meridional direction (Fig. 2b) for all films are observed, indicating high molecular and lamellar orientations.^[13] As shown in Fig. 2(a), these various arc-like diffraction circles from inner to outer are related with different lattice planes for *i*PP, which are the feature of α - and β -crystal. Of note, the diffraction intensity of β (300) emerging in the middle of α (110) and α (040) gradually increases from *i*PP90-0 to *i*PP90-0.2. On the contrary, diffraction intensity of α -crystal gradually weakens with increasing β -NA content. In order to further verify polymorphic composition, 1D-WAXD profiles were achieved, which are presented in Fig. 2(c). From 1D-WAXD profiles, as for *i*PP90-0, reflection peak intensity located at ca. 16.1 for β (300) is relatively weak, which is ascribed to larger number of α -row nuclei induced by strong elongation flow field, thus inhibiting generation of β -crystal. The phenomenon is very different from our previous work.^[10] With elevating β -NA content, reflection peak intensity of β (300) gradually increase, together with the decay of α -crystal peaks located at $2\theta=14.18^\circ$, 16.98° and 18.68° . In light of this, the generation of β -crystal in films is ascribed to the synergistic influence of β -NA and intense elongation field. Moreover, according to the methods in literature,^[16] quantitative calculations of relative β -crystal content (K_β) have been done and the results are summarized in Table 1. Clearly, it can be observed that K_β rapidly increases with increasing β -NA loading and it arrives at a relatively maximum of ca. 0.2 wt%. This is due to the strong heterogeneous nucleation capability of β -NA, which is capable of selectively nucleating β -crystal. Meanwhile, K_α exhibits opposite tendency. This result is consistent with crystalline morphology observed by POM (Fig. S5 in ESI).

The azimuthal intensity curves of α - and β -crystal, i.e., α (110) and β (300) lattice planes are shown in Figs. 2(d) and 2(e). As can be seen from Fig. 2(d), the two reflection peaks at 110° and 255° should be assigned to the “daughter lamellae”, meanwhile, another peak at 180° should be attributed to “parent lamellae” of α -crystal.^[17,18] Analogously, bimodal peaks situated at ca. 110° and 240° are assigned to “daughter lamellae” and the peak located at ca. 180° should be ascribed to “parent lamellae” of β -crystal (see Fig. 2e).^[13,18] Moreover,

there are unobvious parent-daughter structures of *i*PP90-0 and *i*PP90-0.05. Compared with *i*PP90-0.1, reflection peaks intensity from daughter lamellae is strongest for *i*PP90-0.2.^[10] To get further comprehend lamellar branching, the “daughter lamellae” fractions for α - and β -crystal (R_α and R_β)^[19] and K_D (i.e., relative total daughter content for α - and β -crystal) are estimated (Eq. S6 in ESI) and the calculated values are summarized in Table 1. Clearly, R_α and K_D decrease with elevating β -NA content, while R_β is apt to slightly increase, indicating that “daughter lamellae” for α - and β -crystal are prohibited. Additionally, compared with other films, L value of *i*PP90-0.2 is the maximum (Fig. 2f).^[20] As is well known, the lamellar arrangement of β -crystal is loose, leading to larger long period than that of α -crystal.^[21] Therefore, it is reasonable that larger L in *i*PP90-0.2 can be ascribed to higher β -crystal content. Of note, one can observe that there is a slight decrease in X_c after addition of β -NA, which may be interpreted as follows. The thickness of β -nucleated *i*PP films is slightly thinner than that of *i*PP90-0 (i.e., the thickness of *i*PP90-0 is about 30 μm , while the thickness of *i*PP90-0.2 is ca. 28 μm due to the change of viscosity (see Fig. S4 in ESI). Thin film leads to large cooling rate, and thus the effective time is short. This short effective crystallization time allows the formation of imperfect crystal,^[22] thus a slight decrease in X_c for β -nucleated *i*PP films.

The topography of films was observed via AFM, which was carried out in tapping mode. The *ex situ* topography of films upon various β -NA contents are shown in Fig. 3. The top topographies represent amplitude images and those of below represent height images. Clearly, some dense spherulites are observed for *i*PP90-0 and *i*PP90-0.05 (green arrows in Fig. 3a). However, some β -crystal with loose lamellae arrangement is formed by adding β -NA (red arrows Figs. 3c and 3d). In addition, noting that the parent-daughter structure is formed in spherulites for *i*PP90-0.05, which is in accordance with the results in literature.^[23] Meanwhile, one can also notice that lamellar arrangement and size distribution in spherulites are regular and uniform. Moreover, the lamellae interpenetrated into each other can result in enhancement of connection among lamellae. This “cross-hatched” structure influences optical properties, thermal stability, and also tensile properties

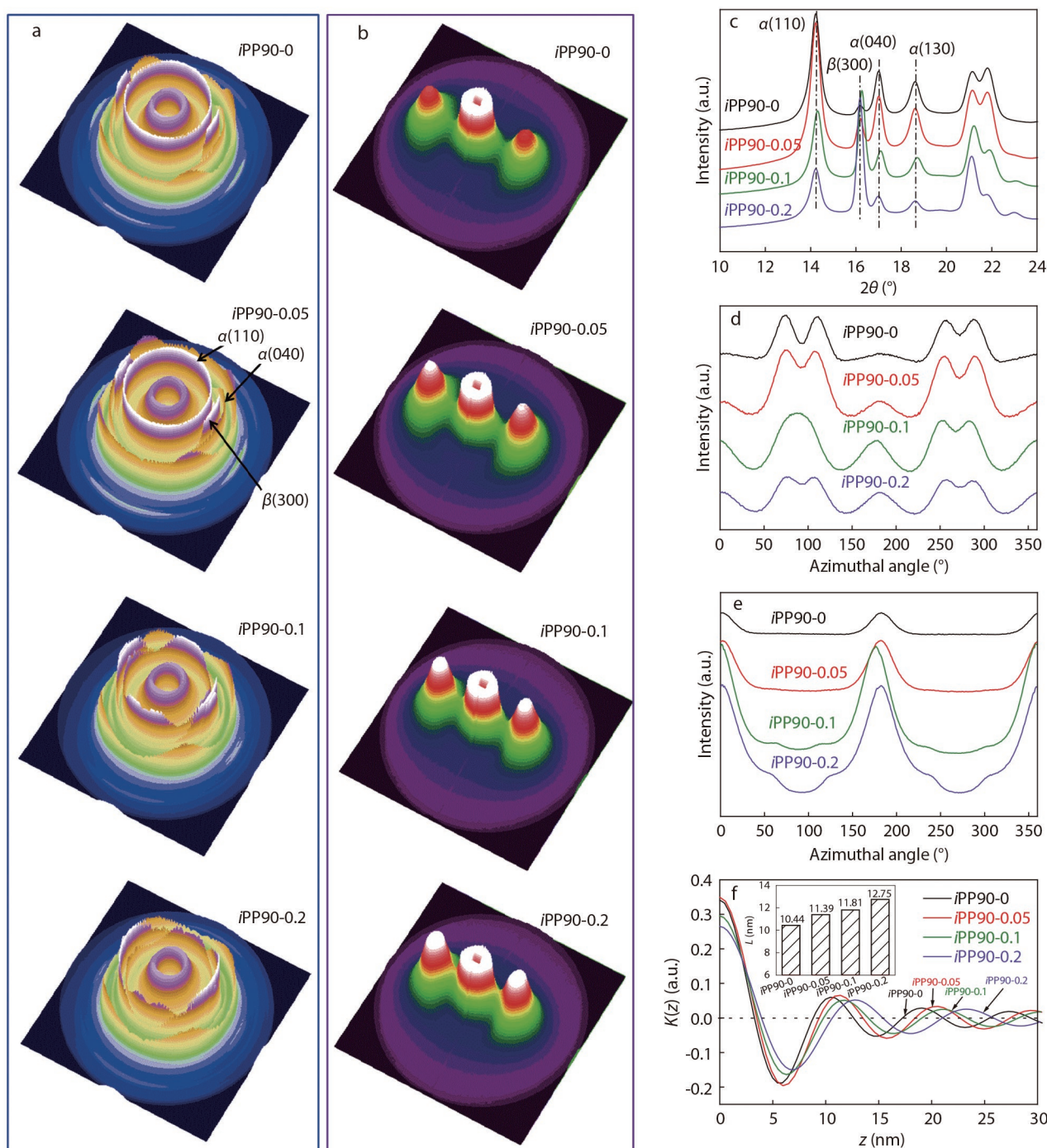


Fig. 2 (a) 3D-WAXD, (b) 3D-SAXS patterns, (c) 1D-WAXD curves, and azimuthal profiles of (d) $\alpha(110)$ and (e) $\beta(300)$ lattice planes and (f) K-z curves of films. The inset in (f) is L values of films.

Table 1 Crystallization parameters of films.

Sample	X_c (%)	K_β (%)	X_β (%)	K_α (%)	X_α (%)	R_α	R_β	K_D
iPP90-0	47.5	1.7	0.8	98.3	46.7	0.8975	—	0.882
iPP90-0.05	46.8	7.0	3.27	93.0	43.53	0.8988	—	0.836
iPP90-0.1	43.7	33.7	14.72	66.3	28.98	0.7465	0.2245	0.571
iPP90-0.2	45.0	50.9	22.87	49.1	22.08	0.7354	0.2574	0.493

of iPP products.^[24–26]

To explore the impact of various β -NA contents on crystal-

lization behaviors of films, the morphological development of films at different temperatures during non-isothermal crystallization were investigated via POM, as shown in Fig. 4. As for iPP90-0, self-assembled iPP chains form individual homogeneous dotted nuclei at about 127 °C and sporadic spherulites appear, which agrees well with the results in literature.^[16] With the further cooling, there are relatively fewer large well-defined and distinct boundaries of spherulites are formed even though a high molecular and lamellar orientation level

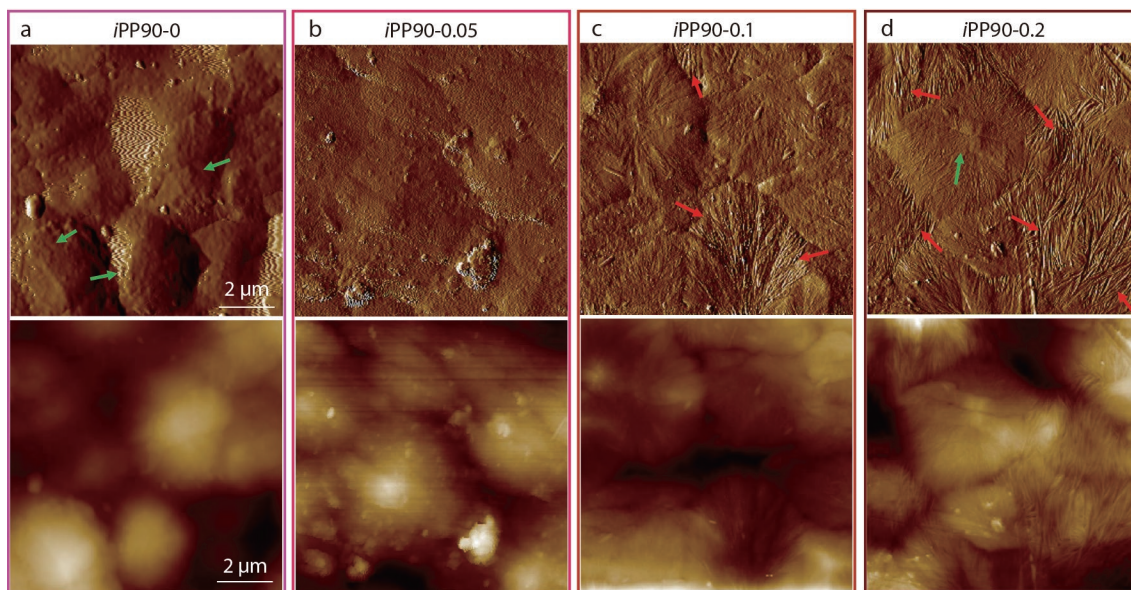


Fig. 3 Tapping-mode AFM photographs of films. The top images represent amplitude images and the bottom images represent height images.

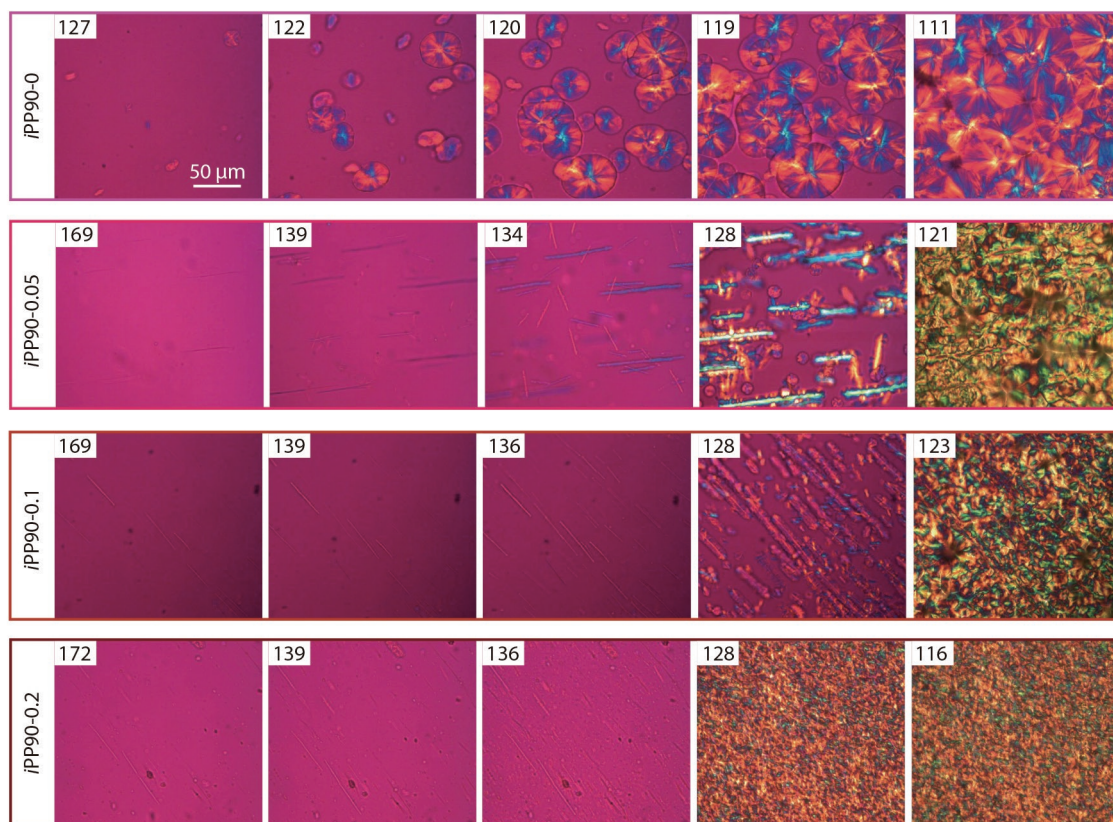


Fig. 4 POM photographs for films at different crystallization temperatures during non-isothermal crystallization. The number represents crystallization temperature.

was identified in *iPP90-0* before melting. This implies that oriented molecular induced by extruded-elongation in *iPP90-0* completely relax upon melting. However, there exists some local order of α -crystal in melt (Fig. S6 in ESI). In our case, β -NA (*i.e.*, WBG-II) is a kind of dispersion type nucleating agents ac-

cording to the melting point of it in polymer matrix. It is established that melting point of WBG-II is as high as 240 °C,^[27] therefore WBG-II granules are indissoluble or half-dissoluble in *iPP* under normal processing conditions (*i.e.*, 190 °C) and it can be spontaneously self-assembled into various agglomer-

ates. Thus incorporation of β -NA can prominently vary crystallization mode, resulting in oriented and anisotropic cylindrites due to the self-assemble behavior of β -NA.^[4] In a word, *i*PP chains occur on needle-like aggregate surface of β -NA, resulting in highly oriented superstructure.^[27] In light of this, it is logical to infer that oriented cylindrites induced via β -NA also exist in final films, which is responsible for tensile properties. Based on the above, due to memory effect of some local order structure around β -NA, some fine and oriented needle-like structures during early stage of crystallization (170 °C) and then cylindrites upon further cooling are formed in β -nucleated films. Additionally, compared with *i*PP90-0, the considerably improved initial crystallization temperature suggests strong nucleation efficiency. Moreover, owing to the enhancement in crystallization sites, final crystal cannot be distinguished from each other and its size gradually declines with increasing β -NA content. Based on the above description, it can be concluded that β -NA can improve the crystallization rate, accompanied by the decrease of spherulite size.

To further elucidate the influence of various β -NA contents on melting and crystallization behaviors of *i*PP, samples with various β -NA contents were investigated via DSC experiment. The melting curves and crystallization curves of films are shown in Fig. 5. Obviously, except for *i*PP90-0, three endothermic melting peaks occur in melting curves. The peaks located at ca. 144 and 151 °C should be related with the fusion of β -crystal, which can be ascribed to the melting of β -crystal with different degrees of perfection and size.^[2,28] That is, the peak located at 144 °C can be associated with the melting of initial β -crystal, whereas endotherm located at 150 °C is related to the melting of perfected or thickened lamellae, which is formed upon heating by partial melting and recrystallization of initially formed β -crystals. Meanwhile the dominant peak around 165 °C is ascribed to the fusion of α -crystal. Moreover, the melting peak of α -crystal slightly increases with elevating of β -NA content, demonstrating the formation of perfect crystal. Noting that there is a small shoulder peak ca. 144 °C for *i*PP90-0, which is consistent with the aforementioned 2D-WAXD results. From Fig. 5(b), β -NA substantially affects the crystallization behavior of the samples. Based on these crystallization curves, crystallization parameters, such as peak crystallization temperature (T_p) and onset crystallization temperature (T_{onset}), can be achieved, which are shown in Fig. 5(c). Clearly, the values of T_{onset} and T_p significantly increase with the increase of β -NA content. For example, T_{onset} and T_p for *i*PP90-0 are 124.6 and 116.2 °C respectively, whereas these values rapidly increased to 135.3 and 126.4 °C for *i*PP90-0.2. The above results verify the efficient nucleating ability of β -NA. In addition, higher T_{onset} suggests a considerable decrease in supercooling (ΔT), which is necessary to start crystallization process.^[10] Therefore, it can offer a relatively longer effective crystallization time, and thus perfect crystal are generated.^[22] The result agrees well with the melting behavior of the samples. Furthermore, L is also related with ΔT , i.e., $L = k \frac{1}{\Delta T}$, where k is a constant.^[29] These results are in good accordance with the calculated L (see Fig. 2f) from K-z curves.

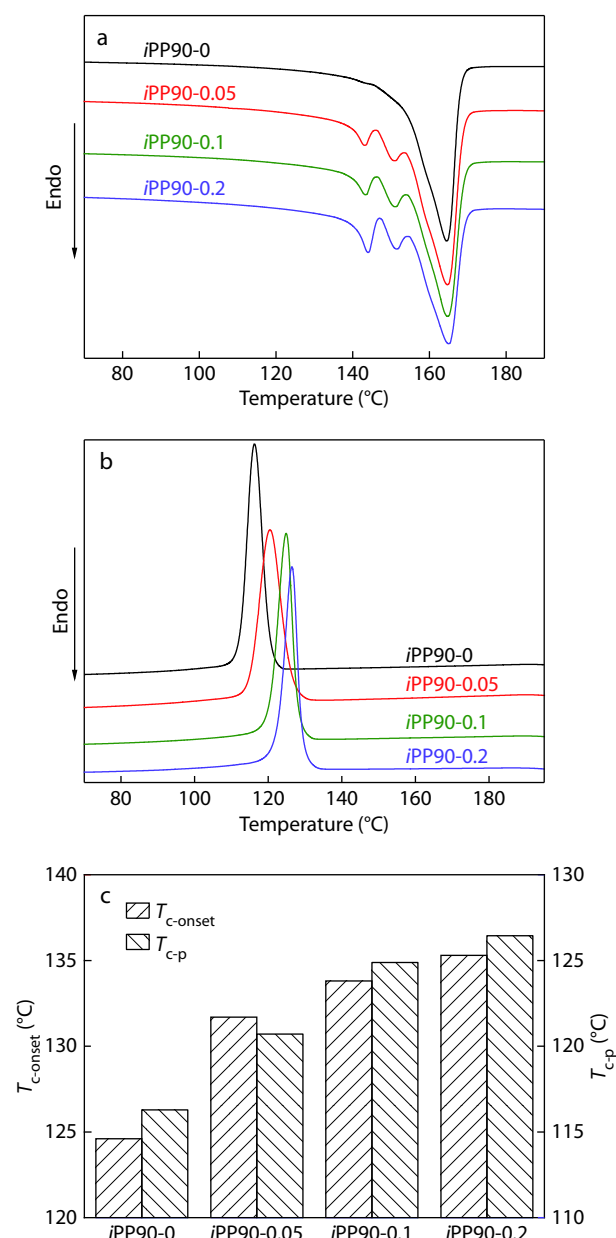


Fig. 5 (a) DSC melting curves, (b) non-isothermal crystallization curves and (c) crystallization parameters of films.

Relationship between Crystalline Structure and Tensile Properties

In our case, the σ of all films is higher than those of 35 MPa in literature.^[12,14,15] This may be ascribed to extremely high orientation (Fig. S7 in ESI)^[9] and obvious lamellar branching structure of α -crystal (Fig. 2d). As is well documented, branching structure is considered as interlocking structure and leads to enhanced inter-lamellar coupling, resulting in the improvement of tensile properties^[30]. Compared with *i*PP90-0, improved toughness of β -nucleated *i*PP films may be ascribed to the following two parts. On one hand, increased K_β upon introducing β -NA is beneficial to improved ϵ and W_b . On the other hand, during the tensile test, the phase transformation from a less (trigonal β -crystal) to a more dense (monoclinic α -

crystal) crystalline structure induced *via* mechanical stress, accompanied with volume contraction in respect to related crystallographic densities, results in toughness improvement.^[31,32] Moreover, this volume contraction prominently contributes to the void formation in general.^[33] Meanwhile, during the deformation of β -nucleated *i*PP films, in addition to intra-lamellar and inter-lamellar slip, lamellar twisting was also observed, which also contributes to the intense voids formation.^[34–36] As is well documented, voids play a crucial role in toughening polymer matrix.^[37] Therefore, in our case, it is understandable that the toughness of β -nucleated *i*PP films is higher than that of *i*PP90-0. In addition, compared with *i*PP90-0, the σ improvement of *i*PP90-0.05 may be attributed to the following reasons. Firstly, larger L results in the increase of molecular chain interactions, that is, improving the fracture resistance.^[38] Thus, the augment of L must be a crucial aspect for enhancement of σ . From Fig. 2(f), it can be found that L value gradually increases with rising β -NA loading, thus leading to a higher σ of *i*PP90-0.05 than that of *i*PP90-0. Secondly, numerous studies have been conducted on strengthening *i*PP matrix with inorganic filler.^[39,40] The β -NA is also a kind of inorganic filler used for reinforcement. Briefly, some oriented *i*PP chains adsorbed on the surface of β -NA can be stabilized and restricted to generate oriented structure (Fig. 4), which is helpful to enhancement of σ . In addition, the σ of *i*PP90-0.1, and *i*PP90-0.2 are lower than that of *i*PP90-0, which is ascribed to the higher content of K_β in β -nucleated samples and stress concentration induced by a large amount of β -NA during testing experiment.

Note that K_β of *i*PP90-0.05 is lower than those of *i*PP90-0.1 and *i*PP90-0.2, while ϵ and W_b as well as σ of the former are higher. It is extensively recognized that β -crystal is beneficial and valid for toughening *i*PP. However, it is interesting that a maximum toughness was also found at certain β -NA.^[41,42] In our case, tensile properties of *i*PP90-0.05 are higher than those of *i*PP90-0.1 and *i*PP90-0.2, which can be explained: on one hand, the toughening effect observed in *i*PP90-0.05 is attributed to the enhancement of connection among lamellae through the generation of “cross-hatched” structure with regular and uniform lamellae in spherulites (see Fig. 3); Moreover, β -NA can disperse uniformly in *i*PP melt and induce generation of β -crystal at lower β -NA content. Above critical β -NA content (*i.e.*, 0.1 wt%), it can spontaneously self-assemble, and thus a deteriorated dispersion may cause stress concentration during testing experiment, resulting in relatively lower tensile properties.^[42] Furthermore, K_β of *i*PP90-0.1 and *i*PP90-0.2 are higher than that of *i*PP90-0.05, which leads to a lower σ of the former. Meanwhile, X_c and K_D gradually slightly decrease with increasing β -NA content, which also results in relatively lower σ for *i*PP90-0.1 and *i*PP90-0.2.

CONCLUSIONS

In summary, *i*PP and β -nucleated *i*PP films filled with various β -NA contents are fabricated *via* melt-extrusion-stretched technology with intended “shear-free” in barrel and die. Subsequently, the impact of various β -NA loadings on crystalline structure and tensile properties of films were investigated. K_β significantly increases with elevating β -NA content, whereas K_D and K_α exhibit an opposite tendency.

Additionally, crystallization rate is elevated along with the reducing of crystal size upon increasing β -NA content. Unexpectedly, tensile properties of *i*PP90-0.05 are higher than those other films. Through comprehensive analysis of crystalline structure, the notable enhancement of tensile properties for *i*PP90-0.05 is attributed to the combined effect of oriented structure, appropriate K_α and K_β values and crystalline morphology. It is noteworthy that the investigation in our case gives in-depth comprehension the correlation between microstructure and tensile properties of β -nucleated *i*PP film fabricated under intense stretching flow field.

Electronic Supplementary Information

Electronic supplementary information (ESI) is available free of charge in the online version of this article at <http://doi.org/10.1007/s10118-021-2589-9>.

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